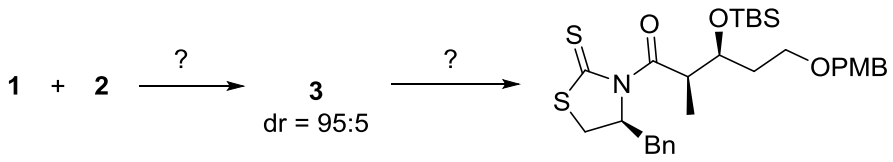
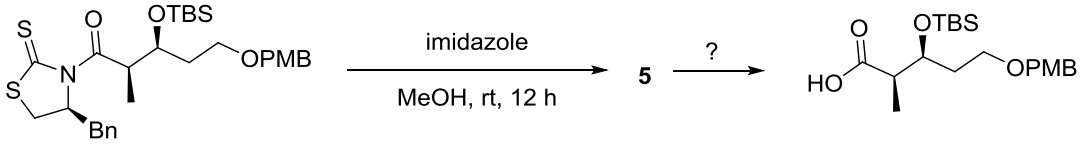
From a total synthesis of a natural product derivative

Problem:



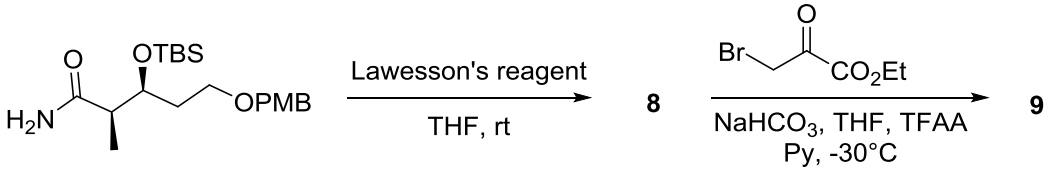
4

1. Please give the reaction sequence with the compounds **1**, **2** and **3** as well as the conditions for the transformations.



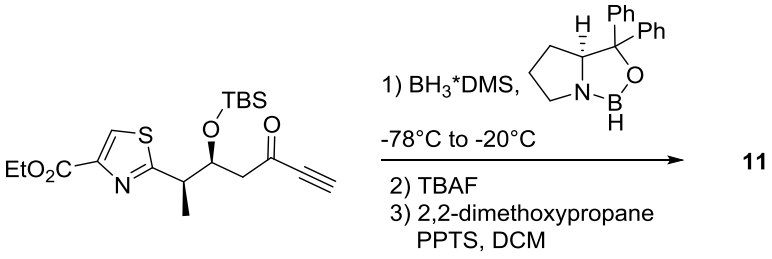
4 **6**

2. What is the product **5** and how is it converted into **6**?



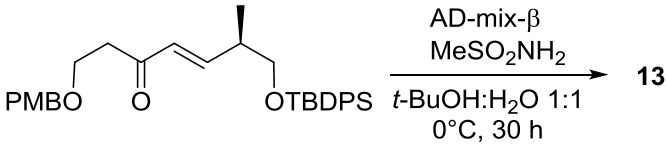
7

3. Please give the products **8** and **9** as well as the mechanism for the transformation of **8** to **9**.



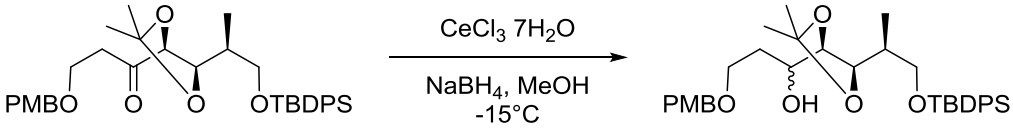
10

4. What is the name of the reaction? Please give the product **11** and a rational for the stereochemistry.



12

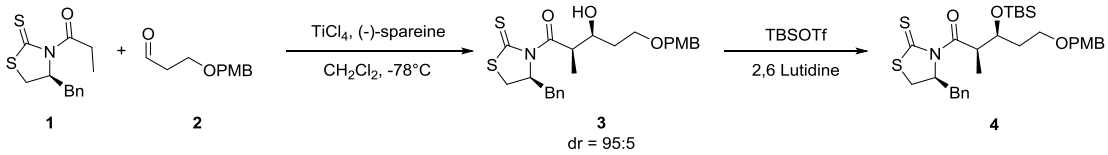
5. What is the product **13** and what is the name of the transformation? Give a mechanism.



14 **15**

6. Give a rational for the reduction and the predicted stereochemistry. Can you explain why Luche conditions were used for the reduction?

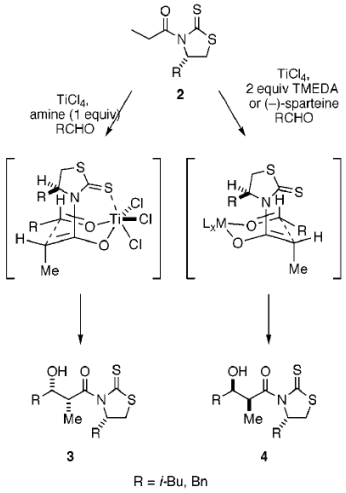
Solution:



1 2 3 4

dr = 95:5

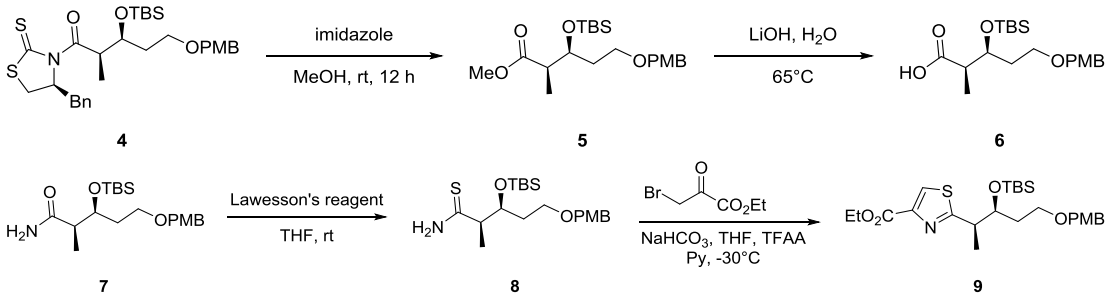
The thiazolidinethione has an increased nucleophilicity which results in the formation of a highly ordered transition state. This leads to the non-Evans syn product. Interestingly the use of 2 equiv. of base leads to the Evans syn product by disfavoring the chelation to the thiocarbonyl by the metal center.



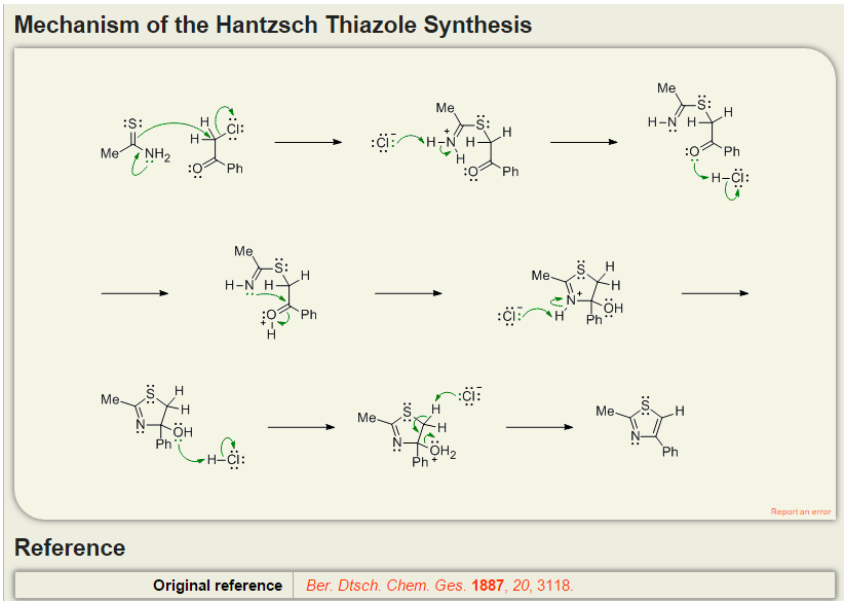
2 3 4

R = *i*-Bu, Bn

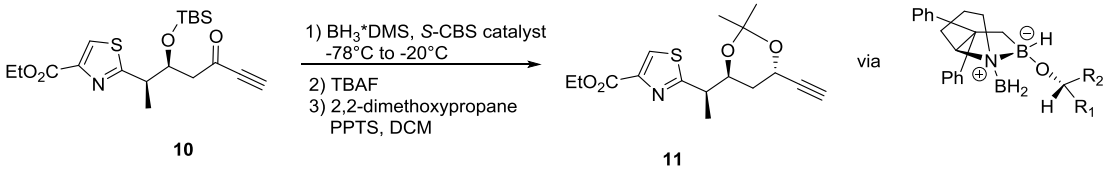
Moreover, the thiazolidinethione are easily removable as well as convertible to other functional groups.



4 5 6 7 8 9

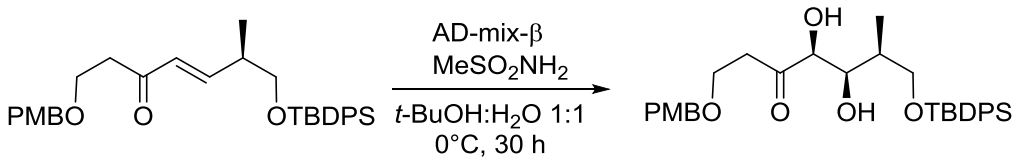


Corey-Bakshi-Shibata-reduction:

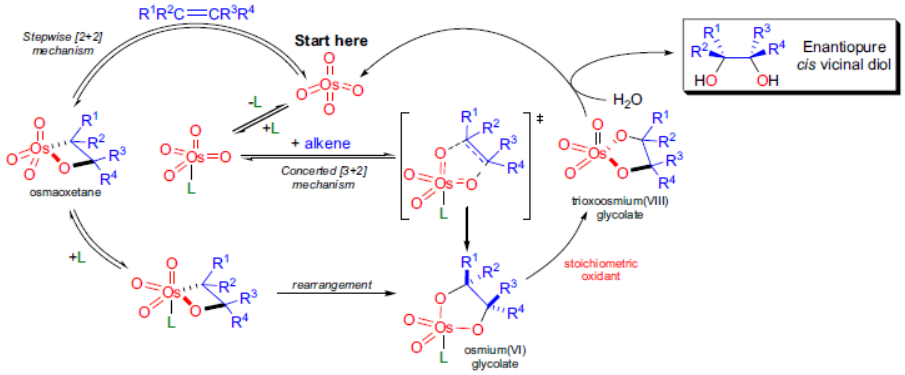


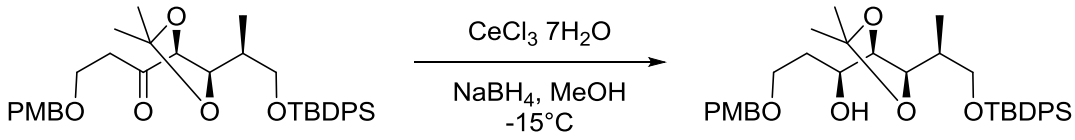
10 11

Sharpless asymmetric Dihydroxylation:



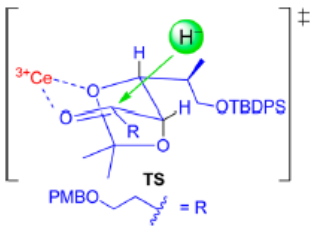
12 13





14 15

Via:



References:

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Keywords:
Total synthesis, stereoselective reduction, dihydroxylation, Hantzsch methodology for thiazole synthesis